Integrated Characterization Studies of Battery500 Consortium

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BAT367

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Overview

Timeline

- Project start date: 10/01/2016
- Project end date: 9/30/2021
- Percent complete: 30 percent

Budget

- Total project funding
  - DOE share $50M
- Funding received in FY 2017: $10M
- Funding for FY 2018: $10M

Core team

Advisors

Barriers

- Barriers addressed
  - Increasing the energy density of advanced lithium (Li) batteries beyond what can be achieved in today’s Li-ion batteries is a grand scientific and technological challenge.

Partners

- Project lead: Pacific Northwest National Laboratory
- Battery500 Core Team: Binghamton Univ., BNL, INL, Stanford Univ./SLAC, Univ. of Texas Austin, UC San Diego, Univ. of Washington
- 15 seedling projects

Relevance and Project Objectives

✓ *Characterization studies to understand the structural changes of high Ni content cathode materials during high rate charge-discharge cycles in thick cathodes (to improve the energy density and rate capability of cathode materials for Li-ion batteries).*

➥ to investigate the structural changes of various cathode materials, especially the NMC materials with high Ni content cycled at different rates, especially at high rate cycling.

➥ to search new approaches to improve the high rate capability of cathode materials including optimize the content of transition metal elements, as well as doping and surface modification techniques.

➥ to provide valuable information about how to design cathode materials with better rate capability for xEV applications.

➥ to develop new *in situ* diagnostic techniques to study the high rate capability cathode materials.

✓ *Characterization studies to understand the capacity fading mechanism during multiple cycling for high energy density materials (to increase the energy density and cycling life of Li-ion batteries)*

✓ *Characterization studies to understand the thermal stability and safety related issues of high Ni content cathode materials.*

✓ *Characterization studies to understand the SEI growing and degradation mechanism of Li metal anode during multiple cycling to increase the cycling life of Li-metal batteries.*

✓ *Characterization studies to understand the interfacial processes relating to the SEI formation and the effectiveness of electrolyte additives, as well as the coating on anode, cathode, and separators.*

Milestones

Month/Year	Milestones
Dec/2017	Design and construct in situ XRD cells for depth –profile studies of thick high Ni content cathodes. Completed.
Mar/2018	Complete the time resolved XRD combined with mass spectroscopy to study the thermal and interfacial stability of high Ni content cathode materials (NMC 622 and 811) during heating. Completed.
Jun/2018	Complete the XAS studies of high Ni NMC cathode multi-cycled at high voltage charge limit to understand the structural stability at high voltage charge. In progress.
Sep/2018	Complete the TXM studies of high Ni NMC cathode multi-cycled at high voltage charge limit to understand the effects of high voltage cycling on the performance fading. In progress.

Approaches

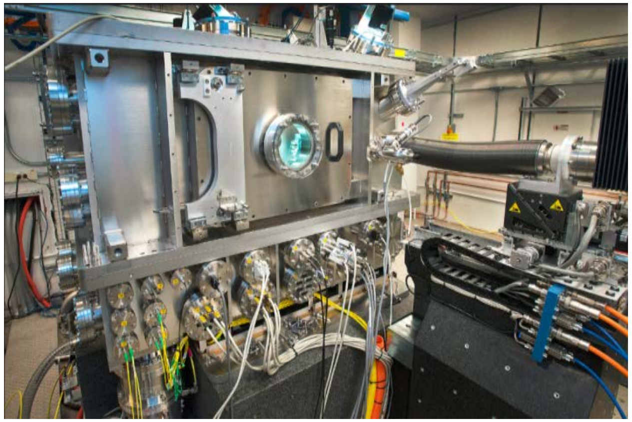
- Using micron-focused beamline at APS to study the depth-profile XRD patterns of phase transitions and other structural changes of thick samples of high Ni content NMC (622) during charge-discharge cycling at different rates
- Using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to study the structural changes of high Ni content NMC (622 and 811) cathode materials during cycling

- Using nano-probe beamline at NSLSII to study the micro-cracks formation and propagation of high Ni content NMC (622 and 811) cathode caused by cycling

- Using x-ray and neutron pair distribution function (x-PDF and n-PDF) techniques to study the O-O bond length changing of high Ni content NMC (622 and 811) during charge-discharge cycling
- Using high resolution transmission electron microscopy (TEM) to obtain multiple dimensional (3D + elemental, valence state, and time) mapping of high Ni content NMC (622 and 811) during charge-discharge cycling.
- Using transmission x-ray microscopy (TXM) to do multi dimensional mapping of cathode materials
- Using Synchrotron based XRD to quantify the dead Li formed during cycling
- Using soft x-ray absorption spectroscopy (s-XAS) and soft x-ray transmission microscopy (STXM) to study the formation and functionalities of solid electrolyte interphase (SEI) in Li-metal batteries

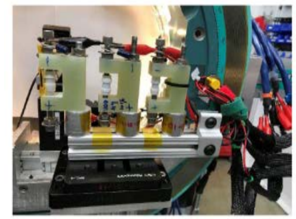
Approach:

The photo of Nano-probe x-ray microscope
At Hard x-ray Nano-probe beamline (HXN) at NSLSII



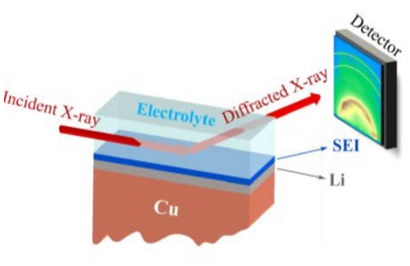
The photo of fast data collection set up with depth-profile XRD capability at advanced photon source (APS) for in situ structural studies for Li-ion battery cathode materials. Three cells can be probed rotationally controlled by computer.

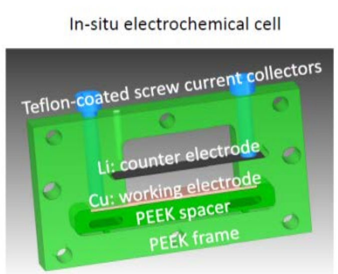
Data collection with *in situ* depth profiling cell



- **3 cells (A, B, C)**
- **6 min / step**
  - ~30 hrs = ~300 steps
- **1 s / scan**
  - 252 scans / step
  - 84 positions / cell
  - 3 vert scans (20 micron)
  - 1 horiz scan (250 micron)
- **Beam: 20 V x 250 H**
- Collected ~75,000 scans over 2 days of beamtime
  - 1,000 GB of data (~1/2 day to copy)
  - Rietveld refinements for about 10,000 scans thus far

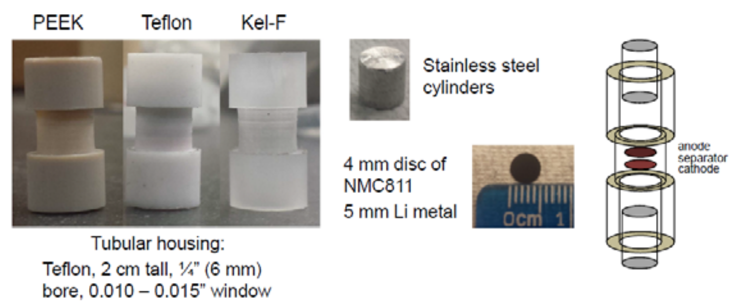
The schematics of using synchrotron based XRD to quantify the formation of dead Li of Li metal anode during cycling





SSRL beamlines 2-1, 7-2, 11-3 Figure courtesy of Chuntian Cao

Design of in situ depth profiling cell



- Modification of RATIX design by Chupas, Chapman, *et al.*
  - Redesigned to address B500 needs: thin films rather than pellets, portability, long lifetime for extended cycling studies, multiplexing

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Technical Accomplishments and Progress

Completed the in situ depth profiling studies using synchrotron based x-ray diffraction to probe the inhomogeneity of thick NMC cathodes (> 140 microns) during cycling at different rates with superb spatial (~20 micron) and temporal (1 second) resolutions. Maps of state of charge (SOC) distribution can be obtained, which is a Key to validate/improve modeling accurately quantified anti-site defects in many NMC samples were studied.

Through synchrotron based nano-probe TXM imaging studies, on NMC811 materials, it was observed that Ni valence state has a gradient from the surface to the bulk. More Ni^{2+} on the surfaces and more Ni^{4+} in the bulk of NMC811 cathode material. Cation inter-mixing was observed at charged state, which may be highly correlated to the reduction of Ni^{4+} resulting from oxygen loss. The micro-cracks formation in bulk was observed by TXM.

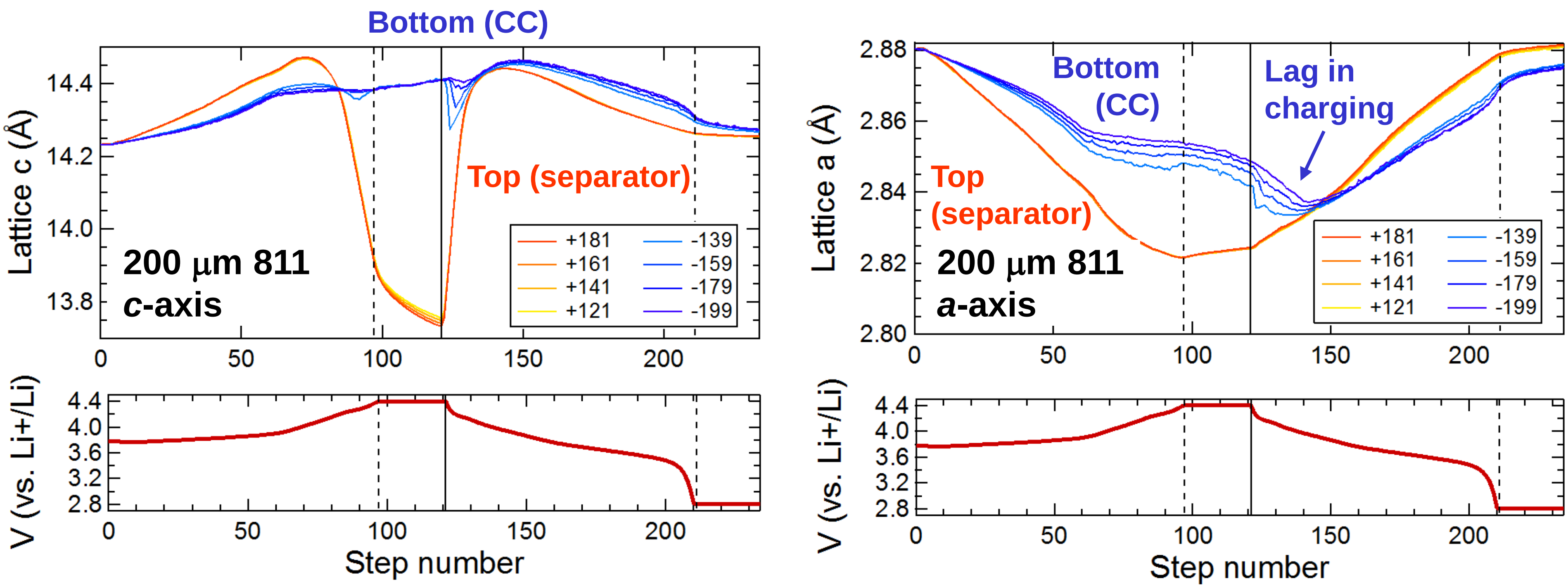
Through high resolution TEM studies, it was found that more nano-sized pores formed in the center of the bulk. The origins of their formation are being investigated. (results obtained from nano-probe X-ray imaging)

The results of in situ synchrotron based XRD studies on Li metal anode can provide valuable information about the amount of Li consumed and dead Li formed during cycling.

Depth Profiling of NMC811 thick cathodes

Peter Khalifah (BNL):	**<u>Zhuo Li</u>**, Gerard Mattei, Liang Yin
Xiao-Qing Yang (BNL):	Seongmin Bak
Ping Liu (UCSD):	Byoung-sun Lee and Zhaohui Wu
Karena Chapman (ANL):	Kamila Wiaderek, Olaf Borkiewicz
Eric Dufeck (INL):	Shrikant Nagpure
Shirley Meng (UCSD):	Chengcheng Fang

C/10 – some top / bottom variation in NMC811



- Top ~75 μm of cathode behave nearly indistinguishably
- Bottom ~75 μm are less active and less homogenous
  - Corresponds to SOC which is 50% lower than top of cathode
- Can see delayed end-of-charge and other oddities in data

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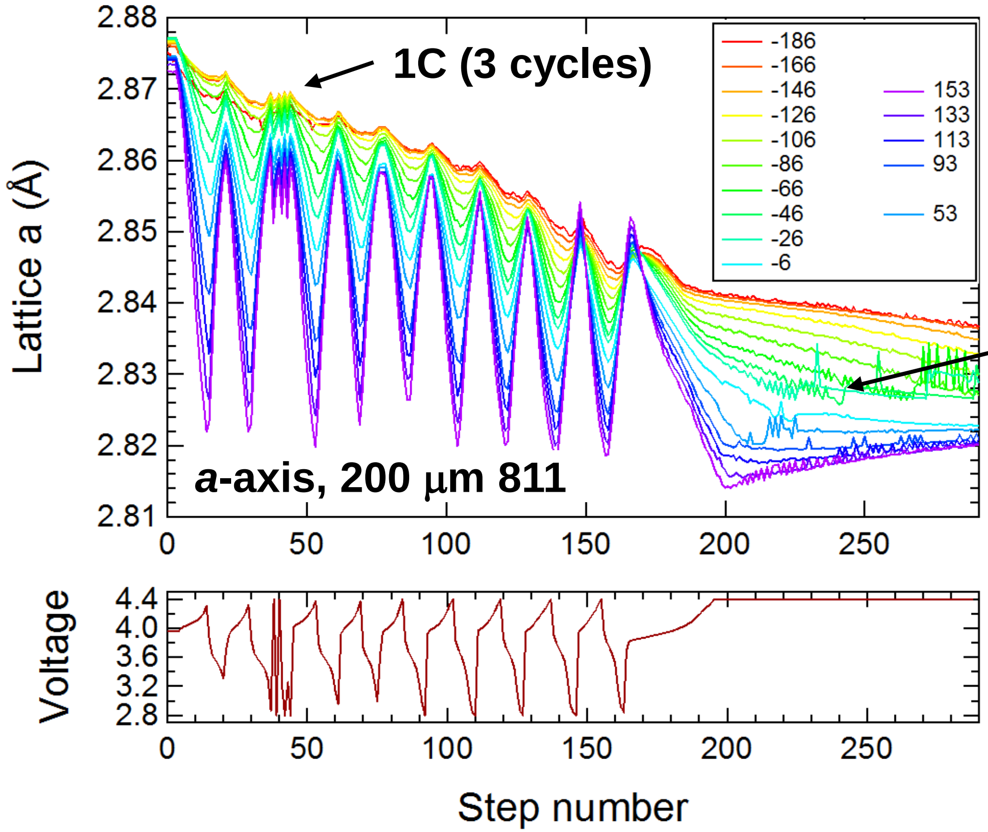
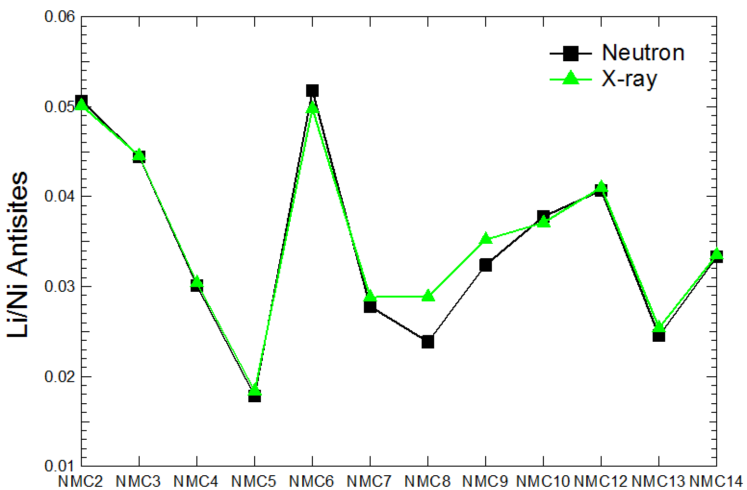
C/3 – severe top / bottom variation in NMC811

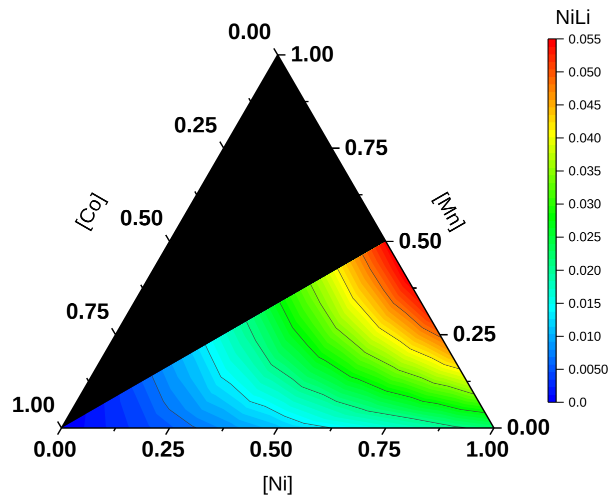


- At higher rate (C/3), thick film shows severe inhomogeneity
  - Variability now seen between top layers of cathode
  - Bottom layer barely sees influence of cyclical applied voltage
  - Bottom layer slowly evolves to higher SOC over ~30 hrs of experiment

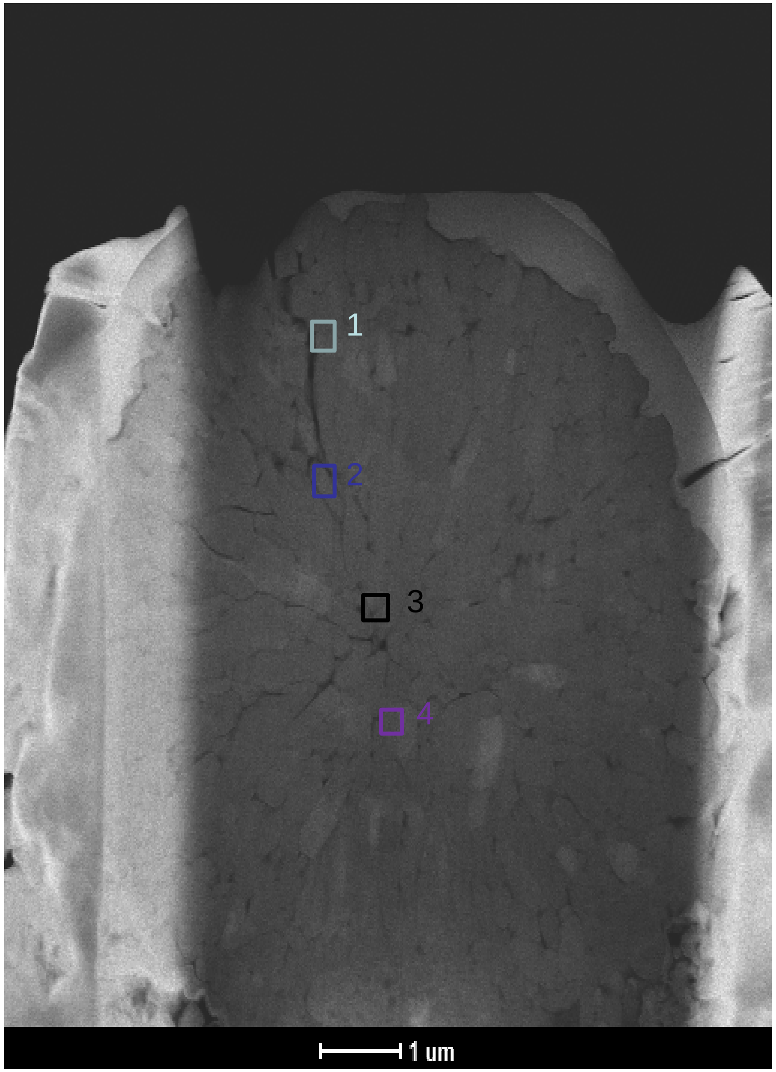
Conclusions

- Depth profiling studies resolve thick electrode inhomogeneity
  - Superb spatial (~20 micron) and temporal (1 second) resolution
  - Many unexpected phenomena seen *in situ*
  - Can extract full SOC distribution -> ***Key to validate/improve modeling***
- Accurately quantified anti-site defects in many NMC samples
  - Can predict defect concentration for arbitrary NMC composition

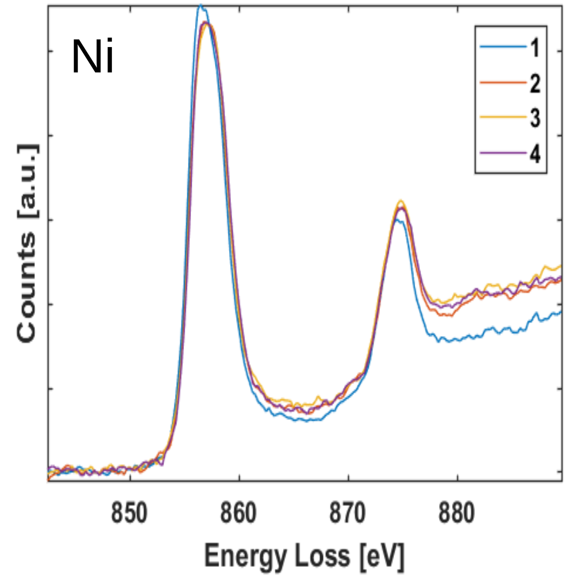


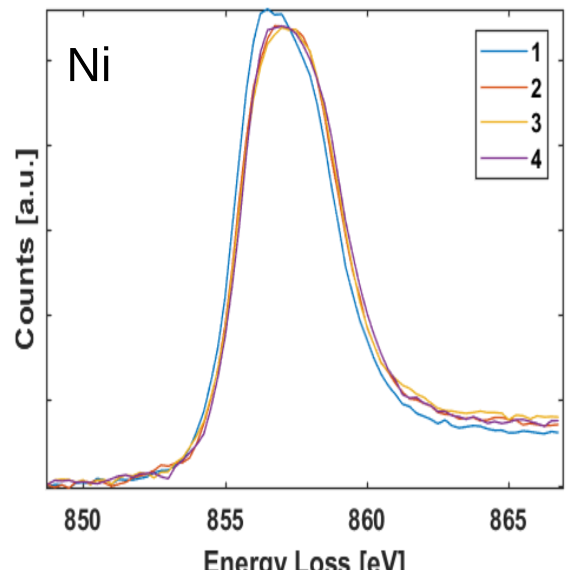


STEM-EELS



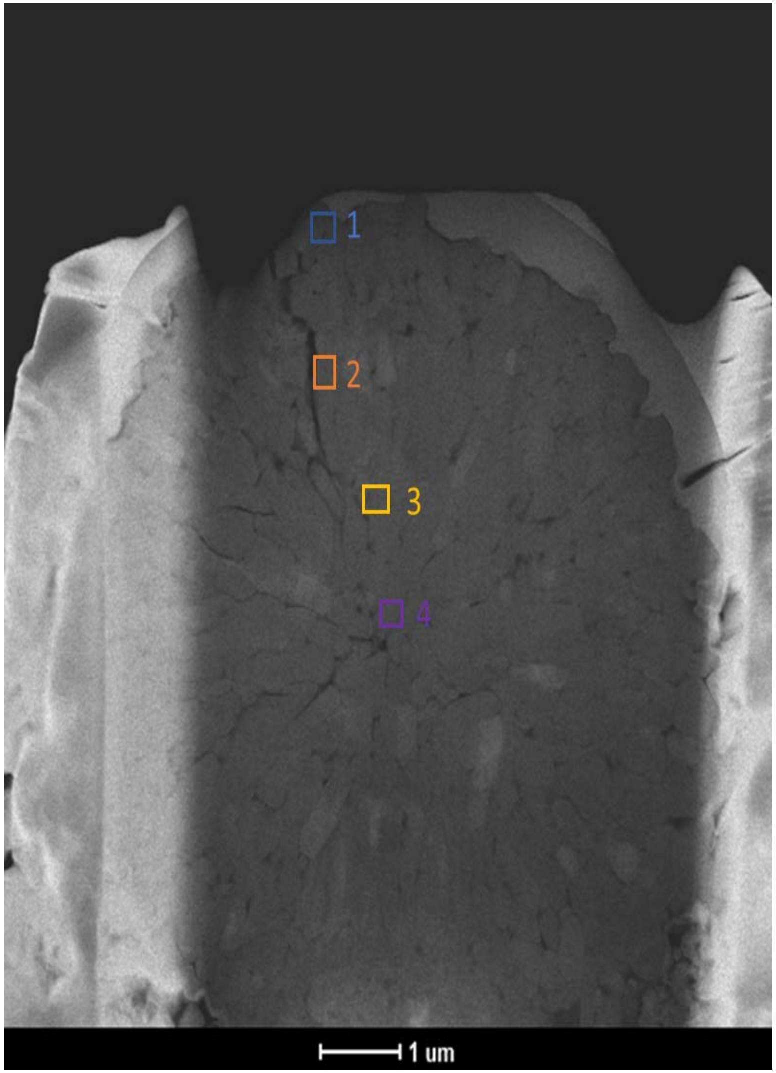
radial crystallographic texture is observed

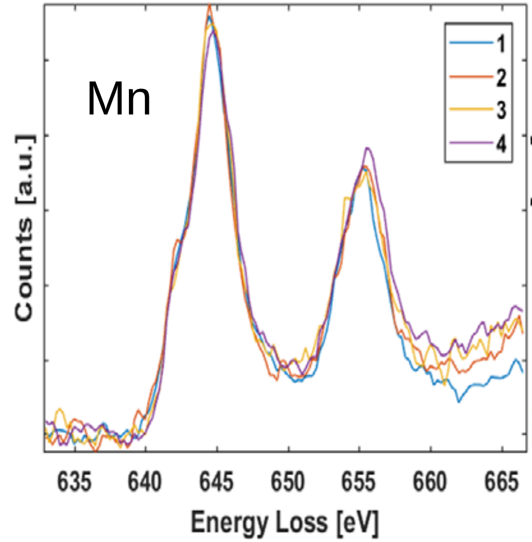


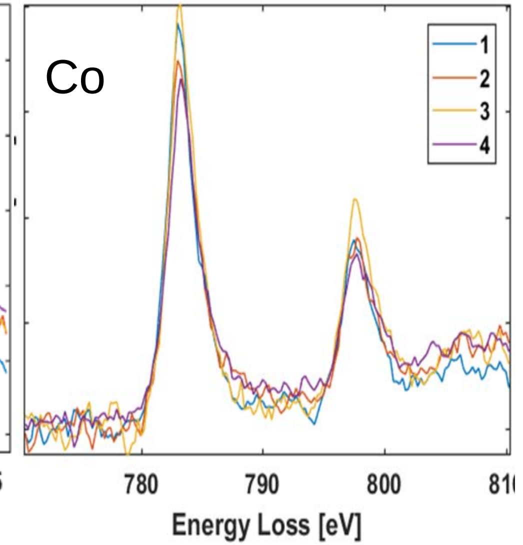


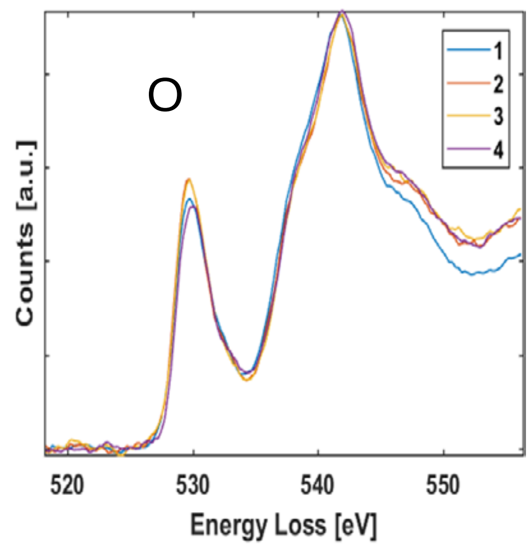
Ni near surface area tends to be at a lower oxidation state than the center bulk.

STEM-EELS



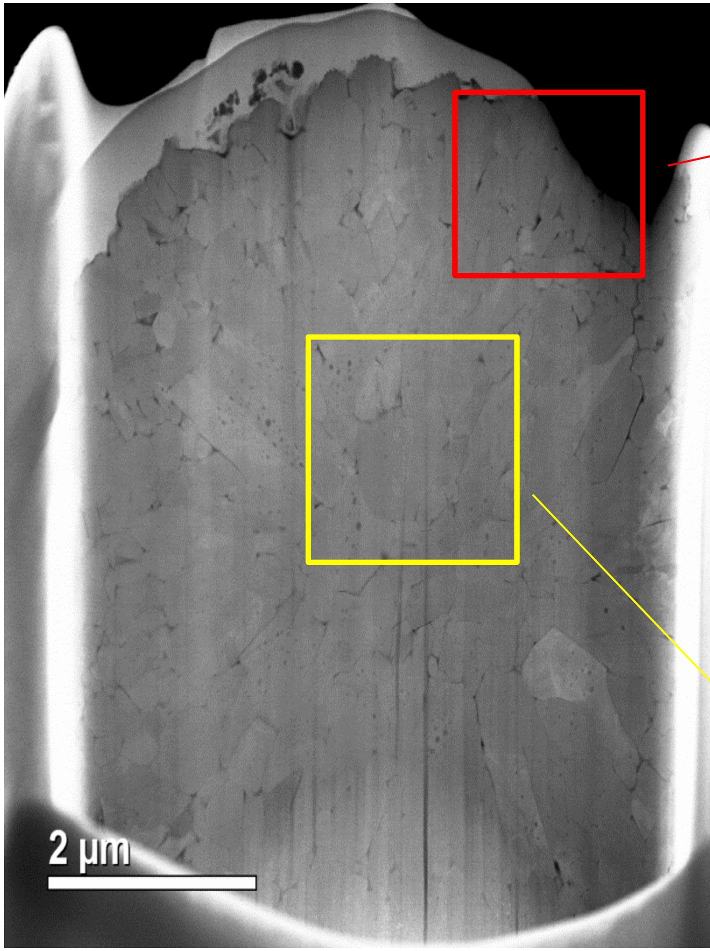


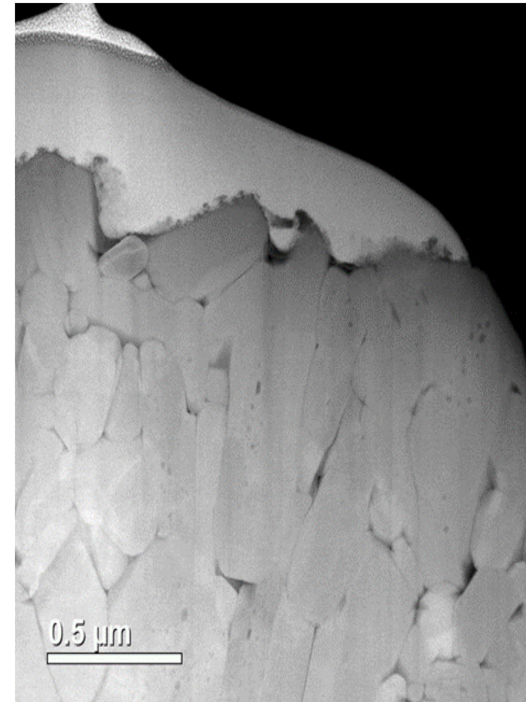


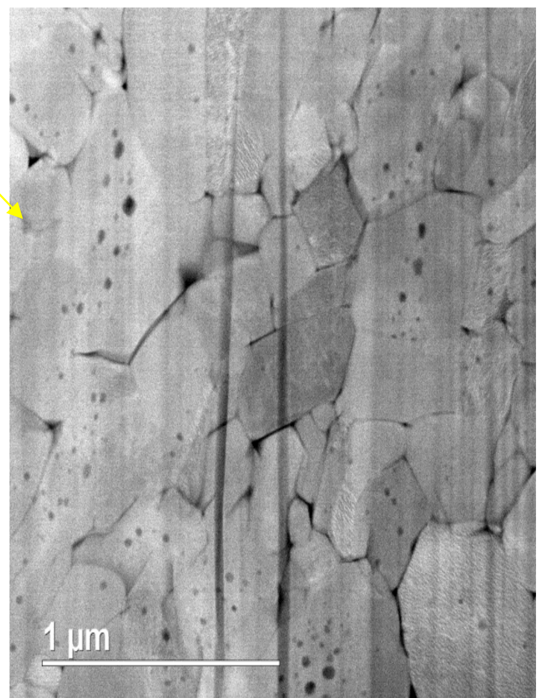


Mn valence at surface and in the bulk are about the same, so as Co.

After 50 cycles, discharged to 4.5 V

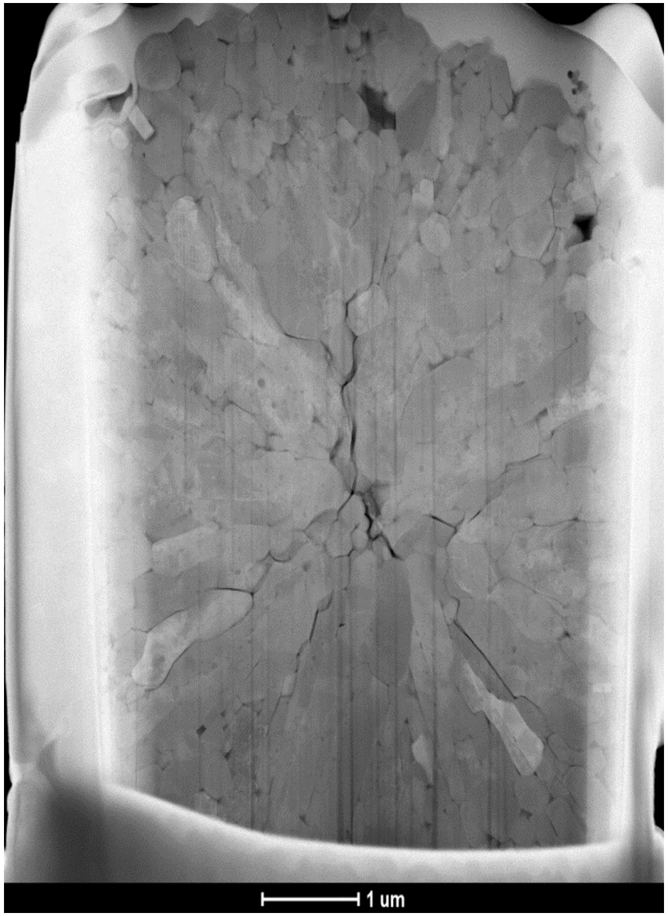




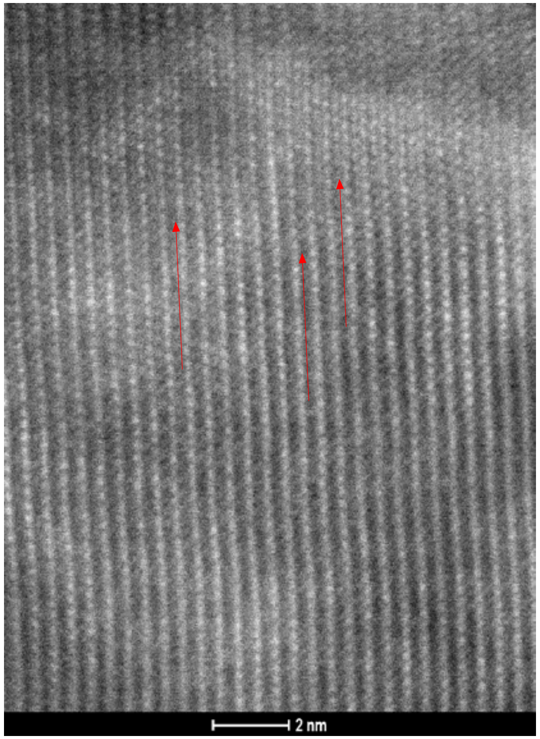


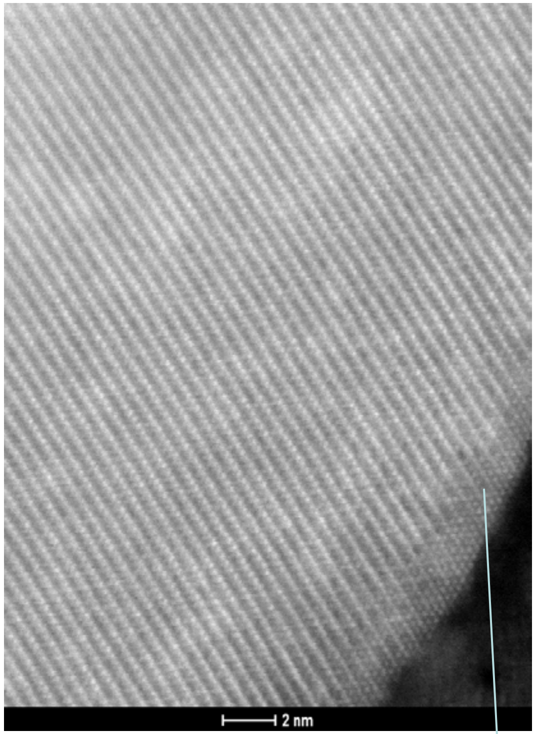
Nano-sized pores formed, higher pore density in the bulk center, may caused by stress created during Inhomogenious lithiation/delithiation

4.4V (charged)
50th cycle



4.4V (charged) 50th cycle





cation mixing

Rock-salt structure near surface

Conclusions of STEM-EELS and TXM studies of NMC811

There's obvious Ni valence gradient in ANL NMC811 cathode material. More Ni^{2+} on the surfaces and more Ni^{4+} in the bulk of NMC811 cathode material.

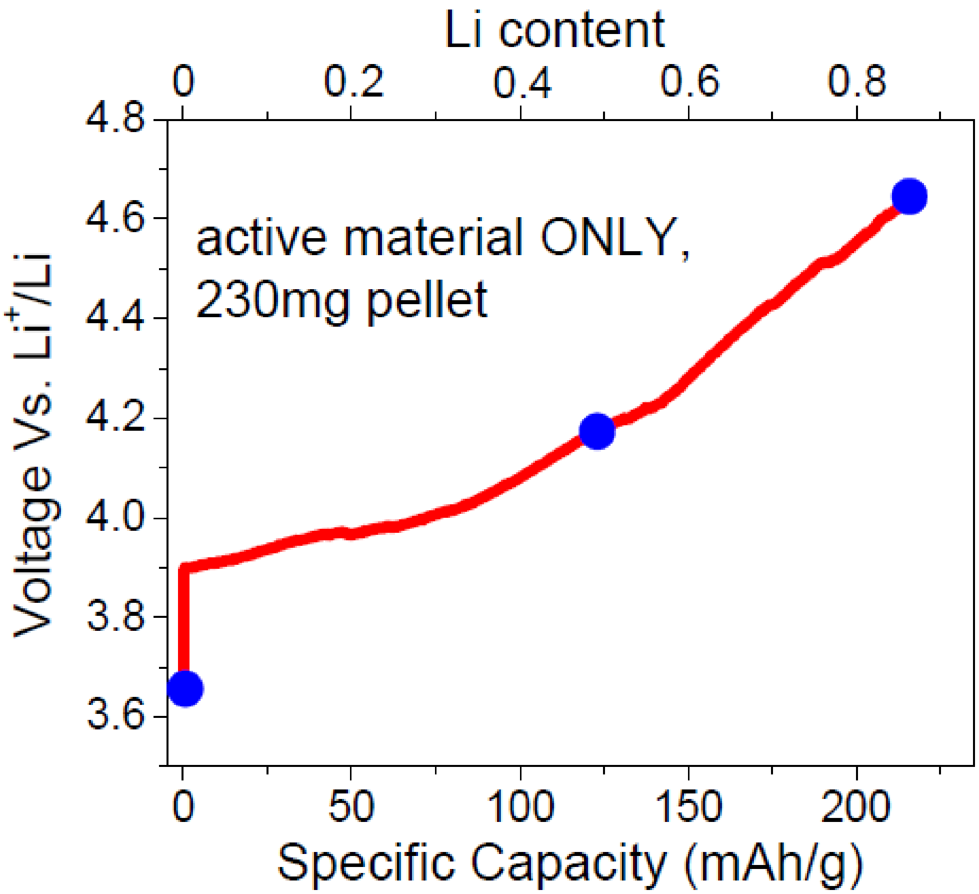
Cation inter-mixing was observed at charged state, which may be highly correlated to the reduction of Ni^{4+} (resulting from oxygen loss.)

More nano-sized pores formed in the center of the bulk. The origins of their formation are being investigated, including: Irreversible delithiation; Oxygen loss; and transition metal migration.

Micro-cracks formed in bulk (results obtained from nano-probe X-ray imaging)

Ni^{2+} may play a positive role in stabilizing the surface composition and structure.

Ex situ neutron PDF Studies of NMC622

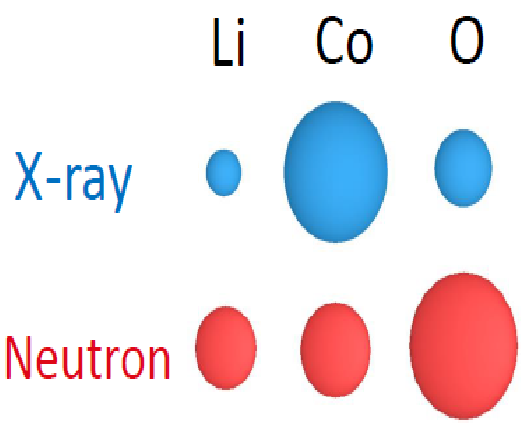


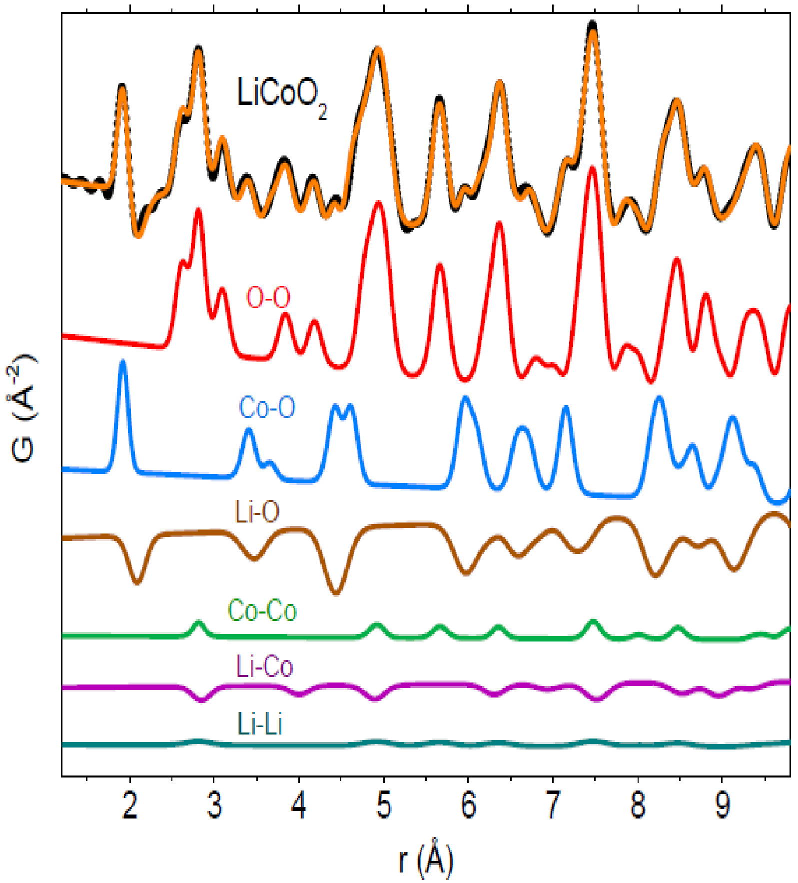
Ex situ nPDF samples were successfully prepared. The current used was 4mA/g.

NOMAD beam line, SNS

.

Experience Gained from Previous nPDF Study on $LiCoO_2$

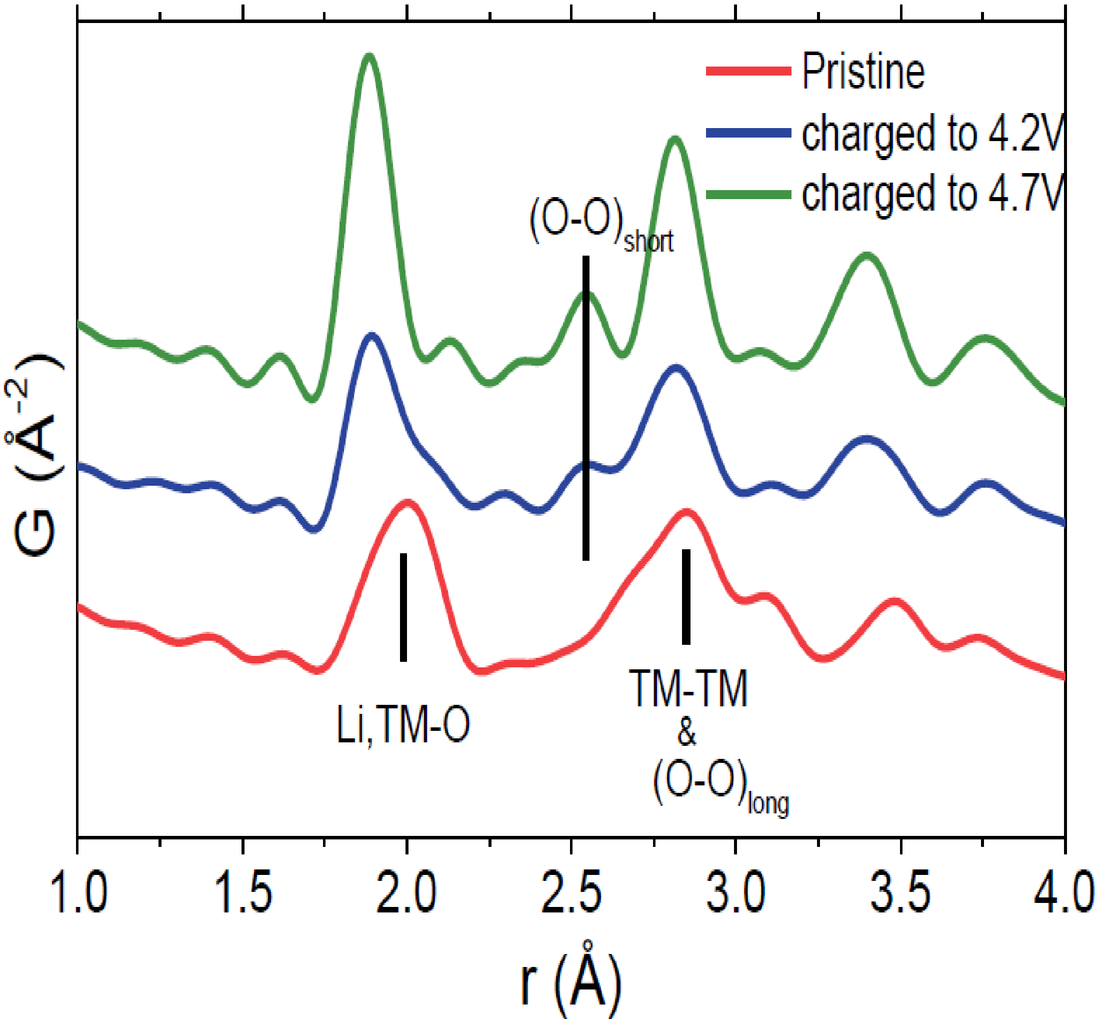




manuscript submitted

O-O pairs make dominant contribution to the neutron PDF data.

Ex situ neutron PDF Studies of NMC622



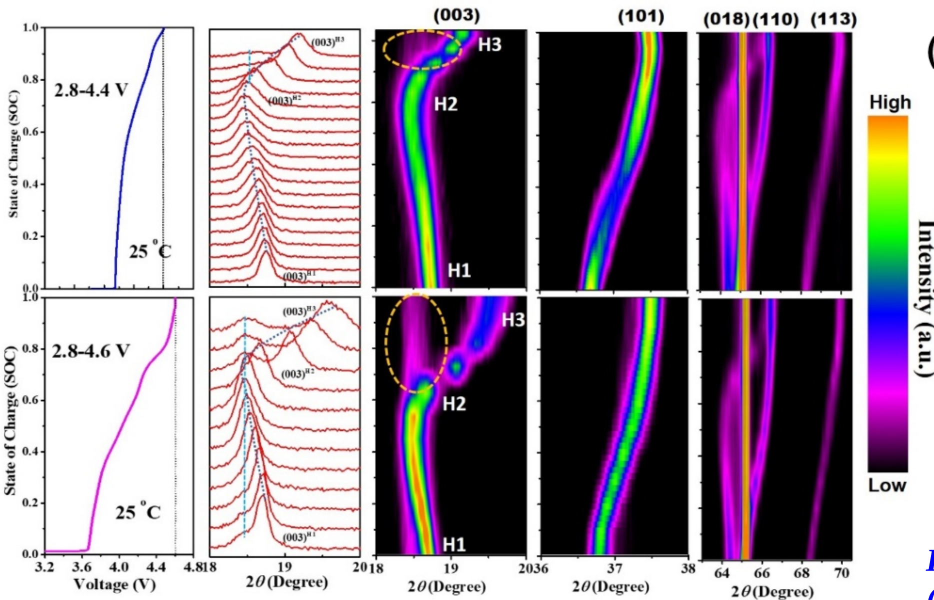
During charging, the shortest oxygen distance shrink to around 2.54 Å, which is **far from the distance of peroxo-like species**. This suggests oxygen loss in NMC622 should be at minimal scale.

Details of comparison between NMC622 and Li-rich in S-M. Bak's talk.

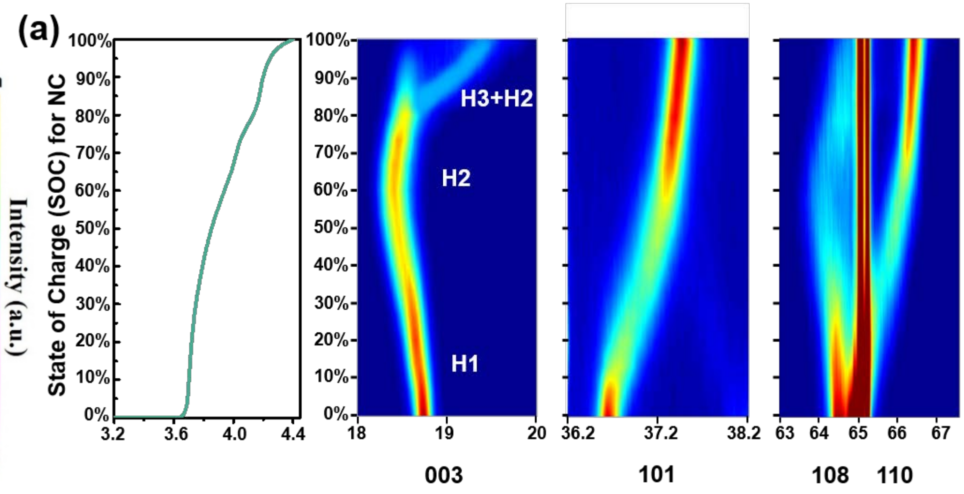
In Situ X-Ray Diffraction

ShanyuWang, MengyuYan, and Jihui Yang, , University of Washington

811: spinel phase at > 4.3 V

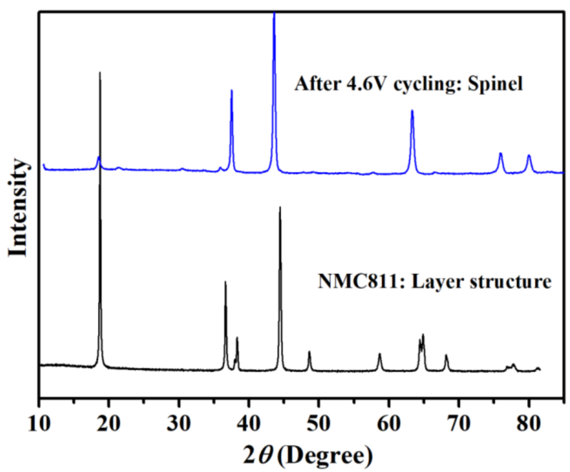


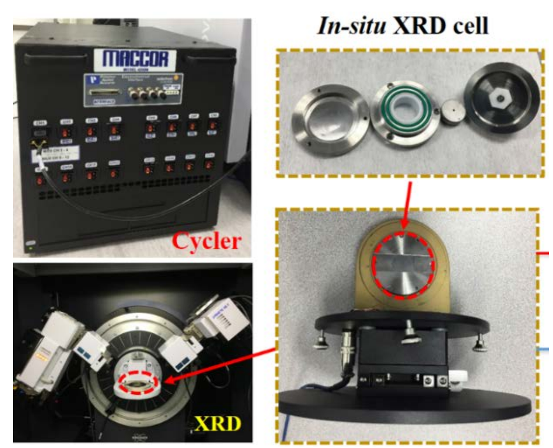
$LiNi_{0.94}Co_{0.06}O_2$: two-phase region at > 4.3 V



In collaboration with UT Manthiram group, manuscript submitted (benefit of Al-doping)

811: transit to spinel phase after 4.6 V cycles





- At high voltages (> 4.3V): metal dissolution and structural instability lead to capacity fading and cell failure

Li metal anodes:
Understanding through X-ray characterization

Natalie R. Geise, Robert M. Kasse, William C. Chueh, Michael F. Toney
SLAC National Accelerator Laboratory & Stanford

X-ray Characterization Approach: Lithium Anodes

SLAC

XAS&STXM:

chemical composition spatio-temporal in SEI

How does SEI form and evolve?

Apply techniques and knowledge to development and design

Where does lithium go?

What makes protection schemes successful?

XRD:

quantification and distribution of 'dead' metallic Li

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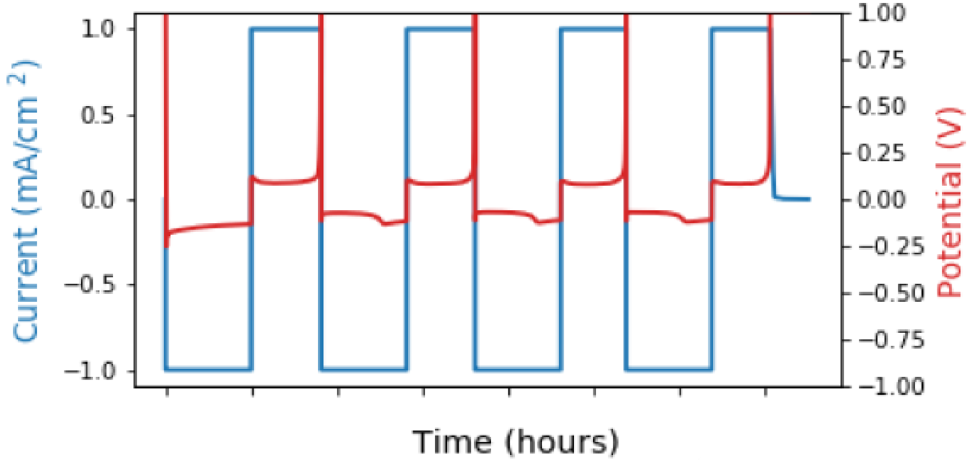
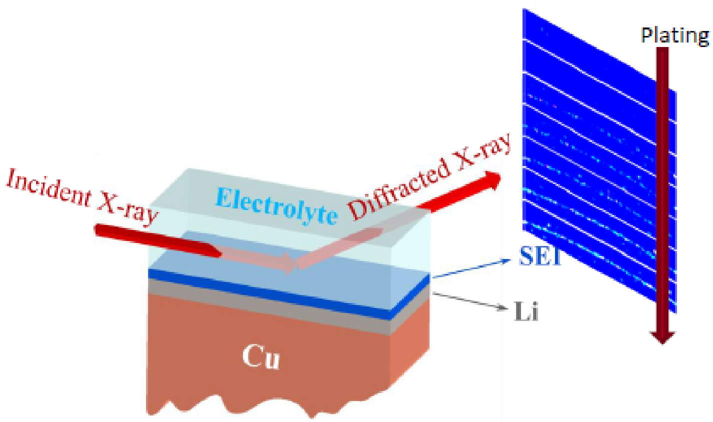
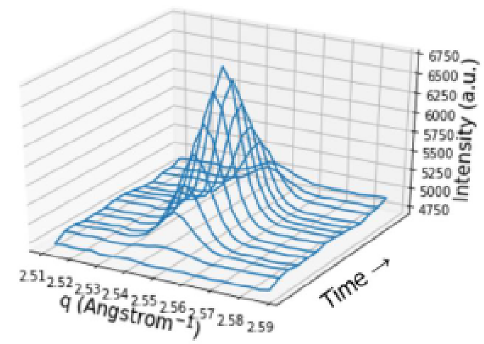
In-situ XRD of Li (110) during plating/stripping







- Electrolyte: 1 M $LiPF_6$ in 1:1 EC/DMC, 1.0 mA/cm^2

SSRL Beamline 7-2 7

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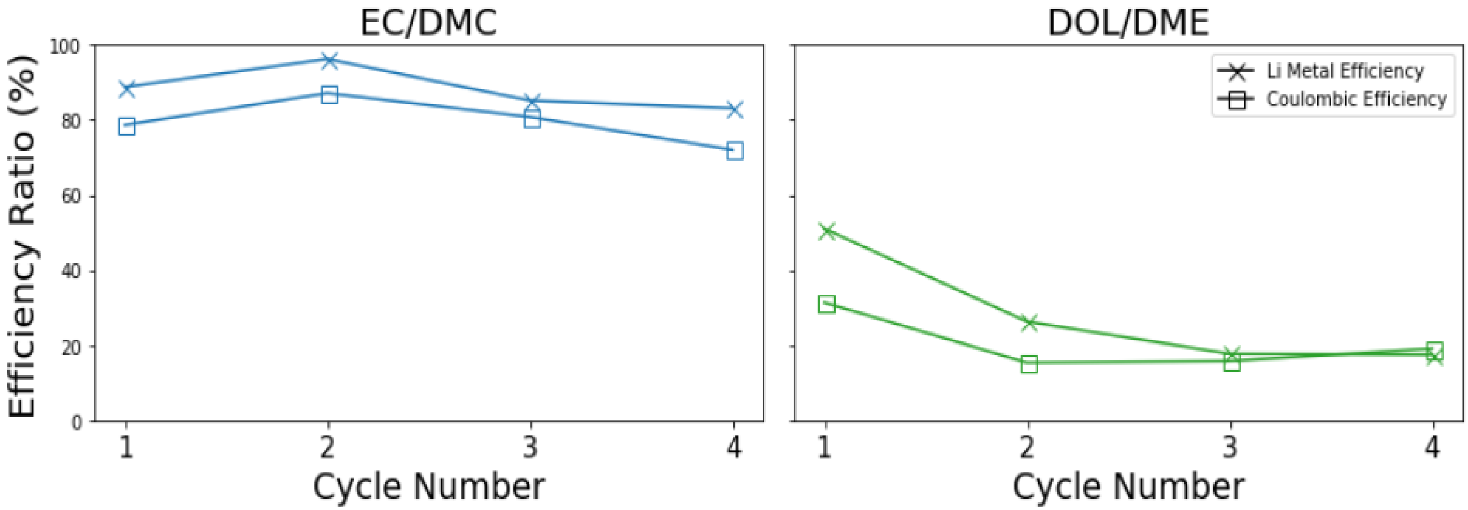
In-situ XRD results: comparison of electrolytes

SLAC

1 M LiTSFI, 0.3 M Li NO_3 in DOL/DME, 1.0 mA/cm^2

1 M $LiPF_6$ in 1:1 EC/DMC @ 1.0 mA/cm^2



- Without pressure, our cell shows worse performance in DOL/DME electrolyte
- Indicates changes in SEI and importance of pressure

SSRL Beamline 7-2

9

Summary for synchrotron XRD studies of Li metal anode

- Quantify the amount of Li consumed and dead Li formed during cycling.

- To answer the question: "Does SEI heterogeneity affect Li nucleation and plating?"

Knowledge obtained can be used to improve the protection scheme design, modeling for Li metal anodes.

Response to 2017 reviewer's comments

This ES367 project was not reviewed in the 2017 AMR review.

Collaborations with other institutions and companies

- All institution members of Battery500 consortium including PNNL, SLAC, INL, Binghamton University, Stanford University, UC San Diego, University of Texas at Austin, and University of Washington

- Argonne National Lab. (ANL)
- Lawrence Berkeley National Lab. (LBNL)
- Army Research Lab. (ARL

- University of Maryland at College Park
- University of Wisconsin at Milwaukee

- Johnson Control Inc.

Remaining Challenges and Barriers

The great challenges and barriers for achieving the 500 wh/kg energy density is significantly improving the reversibility of the Li metal anode. For the characterization team, the main goal is to develop in situ and ex situ characterization tools to monitor the solid electrolyte interphase (SEI) formation; the Li deposition process; the effectiveness of new additives, salts, solvents, as well as new electrolyte systems in suppressing the dendritic Li formation during charge-discharge cycles. The characterization team will be focusing on the efforts in developing the synchrotron x-ray, neutron, and electron based scattering, spectroscopic, and imaging tools for these studies. The results will be communicated with other teams to develop new materials and processes to attack these problems

Proposed Future Work for *FY 2018* and *FY2019*

- FY2018 Q3 Milestone:

Complete the XAS studies of high Ni NMC cathode multi-cycled at high voltage charge limit to understand the structural stability at high voltage charge.

FY2018 Q4 Milestone:

Complete the TXM studies of high Ni NMC cathode multi-cycled at high voltage charge limit to understand the effects of high voltage cycling on the performance fading.

FY2019 work proposed:

Develop and apply neutron pair distribution function (n-PDF) to study the Li-anode and electrolyte interactions

Develop and apply synchrotron x-ray based in situ XRD to study the lithium stripping and deposition process during charge-discharge cycling and the effects of electrolytes and electrolyte additives

Summary

- Relevance

✓ *Characterization studies to understand the structural changes of high Ni content cathode materials during high rate charge-discharge cycling in thick cathodes (to improve the energy density and rate capability)*

✓ *Characterization studies to understand the thermal stability and safety related issues .*

✓ *Characterization studies to understand the SEI growing and degradation mechanism of Li metal anode during multiple cycling to increase the cycling life of Li-metal batteries.*

✓ *Characterization studies to understand the interfacial processes relating to the SEI formation and the effectiveness of electrolyte additives, as well as the coating on anode, cathode, and separators.*

- Approaches

✓ *Using micron-focused beamline at APS to study the depth-profile XRD patterns of phase transitions*

✓ *Using STEM and electron energy loss spectroscopy (EELS) to study the structural changes*

✓ *Using nano-probe beamline at NSLSII to study the micro-cracks formation*

✓ *Using x-ray and neutron pair distribution function (x-PDF and n-PDF) techniques to study the O-O bond changing*

✓ *Using transmission x-ray microscopy (TXM) to do multi dimensional mapping of cathode materials*

✓ *Using Synchrotron based XRD to quantify the dead Li formed during cycling*

- Technical Accomplishments

✓ *Completed the in situ depth profiling studies to probe the inhomogeneity of thick NMC cathodes*

✓ *The micro-cracks formation in bulk NMC811 was observed by synchrotron based nano-probe TXM imaging*

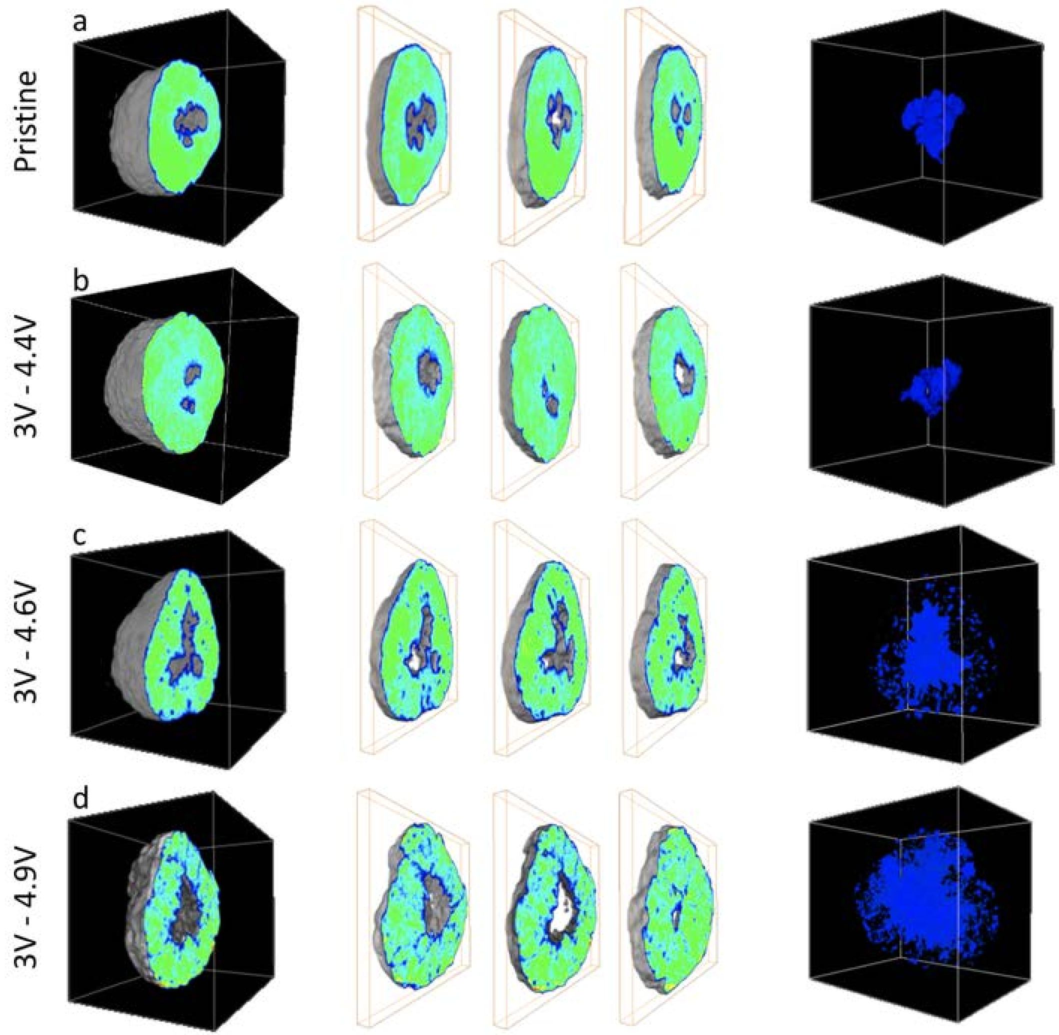
✓ *Through high resolution TEM studies, it was found that more nano-pores are formed in the center of the bulk in NMC811*

- Proposed Future work

✓ *Develop and apply neutron pair distribution function (n-PDF) to study the Li-anode and electrolyte interactions*

✓ *Develop and apply synchrotron x-ray based in situ XRD to study the lithium stripping and deposition process and the effects of electrolytes and electrolyte additives*

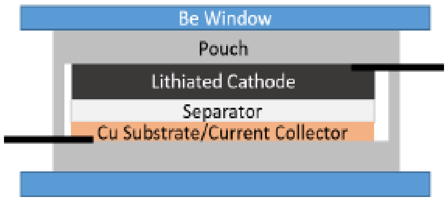
Transmission x-ray microscopy (TMX) images of NMC622 cathode samples charged to different voltages

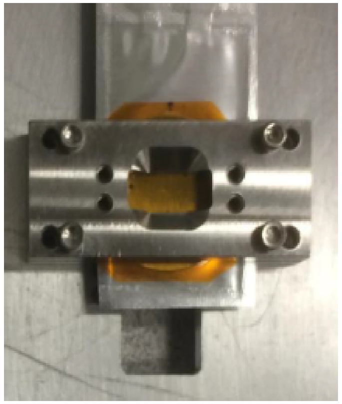


Continuing Work

SLAC

- Pouch Cell Design – upcoming beamtimes





- X-ray microscopy/microdiffraction at APS: further analysis and refinement of cell design for microdiffraction

- Lithium/dead lithium quantification with known protection systems –Jason Zhang group's electrolytes, Cui & Bao group coatings (polymer, LiF, BN), P Liu